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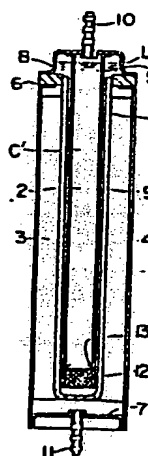
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54 Sodium-sulfur battery.

57 The present invention relates to an internal structure of cathode of a sodium-sulfur battery, and particularly to a sodium-sulfur battery which is improved to extend its life by keeping low the resistivity of sodium ion conductive solid electrolyte (1) through elimination of impurities in sodium which acts as a cathode active substance (2). That is, although it has hitherto been known that the solid electrolyte (1) is deteriorated by impurities such as K^+ , Ca^{2+} and the like in sodium which is the cathode active substance (2), a method for improving this has not been known. According to this invention, a porous adsorbent (12) is immersed in sodium which is the cathode active substance (2) to eliminate the impurities in the sodium, resulting in extension of the battery life.

FIG. 1



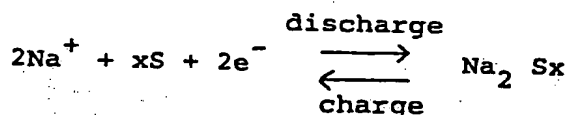
SODIUM-SULFUR BATTERY

1 BACKGROUND OF THE INVENTION

The present invention relates to an internal structure of a cathode of sodium-sulfur battery, and particularly to a sodium-sulfur battery which is improved to extend the life by keeping low resistivity of sodium ion conductive solid electrolyte through elimination of impurities in sodium which acts as a cathode active substance.

The sodium-sulfur battery is a high-temperature secondary battery in which the solid electrolyte permitting only sodium ion to pass through is interposed such that molten (liquid) sodium acting as a cathode active substance is disposed in one side and molten sulfur acting as an anode active substance is disposed in the other side, whereby charge and discharge may be carried out at a temperature range of about 300°C to 350°C.

Such charge and discharge reactions are represented by:



20 In discharge, an atomic sodium as the cathode active substance liberates electrons to become sodium ion, which passes through the barrier of the solid electrolyte to

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1 react with the sulfur of the anode active substance and
to produce the sodium polysulfide ($\text{Na}_2 \text{S}_x$). In charge,
the sodium polysulfide ($\text{Na}_2 \text{S}_x$) is separated to the
sodium (Na) and the sulfur (S) by applying the negative
5 voltage larger than the voltage of opened circuit.

Fig. 2 illustrates an example of the conventional sodium-sulfur battery. Referring to the drawing, the sodium-sulfur battery consists of the molten sodium
2 of the cathode active substance and the molten sulfur
10 3 of the anode active substance filled inside and
outside of a tubular solid electrolyte 1, respectively.
Since the molten sulfur 3 has no electronic conductivity,
a porous carbon fiber is impregnated with the molten
sulfur 3 in order to give the electronic conductivity
15 thereto. An anode container 4 in which the molten
sulfur 3 is enclosed and a cathode tube 5 in which the
molten sodium 2 is enclosed have the function of
electrode, respectively, and the anode container 4 and
the cathode tube 5 are connected in an insulated
20 manner by an α -alumina 6 which acts an insulating
material.

Also, an anode cap 7 secured to the anode
container 4 and a cathode cap 8 secured to the cathode
tube 5 have the function of electrode as well as the
25 anode container 4 and the cathode tube 5. A porous
metal fiber 9, which is inserted into the molten
sodium 2, has the function of retainer of the molten
sodium 2 for preventing a drastic exothermic reaction

1 of the molten sodium 2 and the molten sulfur 3 when the
solid electrolyte 1 is broken. To the cathode cap 8 is
secured a sodium injection tube 10 for injecting sodium
into the cathode tube 5. "C" designates a cathode
5 which consists of the molten sodium 2 and the metal
fiber 9. "L" designates a liquid surface of the sodium
2. The solid electrolyte 1 in the sodium-sulfur
battery is a main part which influences the performance
of battery, and materials called β -alumina or β'' -alumina
10 are used as such electrolyte, which can be produced by
mixing Na_2O , Li_2O and the like with usual alumina
powder, ~~molding the mixture under~~ an elevated pressure,
followed by sintering at a high temperature. As to the
characteristics of the solid electrolyte 1 for the
15 sodium-sulfur battery, it is required that it has high
density and no gas permeability, the mechanical strength
is high, the ion conductivity is large, the resistance
of grain boundaries (which means that the
flow of sodium is biased between the grains so that
20 it is hard to flow.) is low and the electric conductiv-
ity is good, the distribution of grain size is
uniform, and the grain is fine and not deteriorative.
The main cause of deterioration of the solid electrolyte
1 which has the particular characteristics as mentioned
25 above, is the influence of impurities such as potassium
ion (K^+), calcium ion (Ca^{2+}) and the like contained in
the molten sodium 2.

The electric conductivity of the solid

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1 electrolyte 1 with respect to the sodium ion (Na^+) is
deteriorated remarkably due to the existence of
impurity ions (K^+ , Ca^{2+} , etc.) contained in the molten
sodium 2 as mentioned above, resulting in the high
5 internal resistance of battery. Also, in the crystal
structure of the solid electrolyte 1 (β - Al_2O_3 , β'' - Al_2O_3 or the like) consisting of the sodium ion (Na^+),
the substitution of the sodium ion (Na^+) by the
impurities (K^+ , Ca^{2+} , etc.) causes the change of volume
10 of the crystal single particle. The change of volume
results in that stress is produced inside of the solid
electrolyte 1 or near the surface thereof so that it
accelerates the deterioration of the solid electrolyte
1 because the crystal particles are different in size
15 from the point of probability theory.

The deterioration mechanism of the solid
electrolyte used for the sodium-sulfur battery is due
to the damage when the sodium ion permeates through or
to the action such as extreme increase of resistance.
20 These are much influenced by the impurities contained
in the sodium.

The deterioration phenomena of the solid
electrolyte due to the impurities are described in the
"Kagaku Kogyo" (Chemical Industries), August, 1980, page
25 88, " β -alumina (2)". However, it refers to neither the
countermeasure nor the method of improvement for such
deterioration.

Furthermore, the Japanese Patent Publication

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1 No. 8552/83 discloses the improvements of strength and
non-corrosiveness of the solid electrolyte for sodium-
sulfur battery, but it describes neither the influence
due to the impurities in sodium nor the method of
5 improvement.

SUMMARY OF THE INVENTION

This invention has been done in view of the
above mentioned circumstances, and is aimed to provide
a sodium-sulfur battery in which the sodium ion
10 conductive solid electrolyte is prevented from deterior-
ation, whereby the battery life is remarkably extended.

Next, the basic principle of this invention
is described.

The life of the whole system of sodium-sulfur
15 battery is often decided by deterioration phenomenon of
the sodium ion conductive solid electrolyte itself.
That is, the solid electrolyte through which a certain
quantity of electric current has passed, sometimes
generates micro-cracking or shows an action that the
20 value of resistance increases extremely. Thus, in the
deteriorated sodium-sulfur battery, the solid electro-
lyte is easy to break and at the time of breakdown, the
sodium which has high chemical reactivity reacts with
sulfur in a short time to produce exothermic heat.
25 This is not preferable from an aspect of safety. One
of the causes of deterioration of the solid electrolyte
used in the sodium-sulfur battery is largely due to

1 the influence of impurity contained in the sodium.
Even the high purity sodium contains a very small
amount of impurities such as potassium, calcium,
hydrogen, oxygen boron and the like. These impurities
5 change the composition of the solid electrolyte and the
volume of crystal particle by substituting for the
sodium ion and at this time, a stress occurs near the sur-
face where many single crystal grains whose composition
has been changed exist, and it breaks the solid elec-
10 trolyte. Further, the impurities have properties that
they penetrate into the grain boundaries of
the solid electrolyte to increase the resistance of
grain boundaries and to accelerate the
deterioration and damage in the grain bound-
15 aries. Accordingly, it is necessary for improving
the battery life to eliminate the impurities present in
sodium. Also, a marked extension of battery life can
be expected by eliminating the impurities mentioned
above. For achievement of the above-mentioned object,
20 i.e. the extension of battery life by preventing the
ion conductive solid electrolyte from deterioration,
based on the principle described above, the sodium-
sulfur battery of this invention is characterized in
that a porous adsorbent is immersed in the sodium which
25 acts as a cathode active substance.

As the porous adsorbent, porous adsorbents
such as carbon, graphite, alumina and the like, and
high purity porous active carbon are preferable.

1 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatic illustration in cross section of an embodiment of sodium-sulfur battery according to this invention; and

5 Fig. 2 is a diagrammatic illustration in cross section of an example of the conventional sodium-sulfur battery.

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DESCRIPTION OF THE PREFERRED EMBODIMENT OF THE INVENTION

15 Fig. 1 shows an embodiment of this invention. In Fig. 1, numeral 1 designates a β "-alumina solid electrolyte which has high electric conductivity with respect to sodium ion. Since the solid electrolyte 1 has high insulation property with respect to the elec-
20 tronic conductivity, it retains separately sodium 2 which is a cathode active substance and sulfur 3 which is an anode active substance without self-discharging. The sodium in a solid electrolyte tube is separated into a sodium ion and an electron on the surface of
25 solid electrolyte. When an external circuit is not connected between a cathode and an anode of the battery, the sodium ion does not transfer because of the negation

1 of electric field due to the space charge potential, but
when there is a path electrically connecting between the
cathode and the anode outside, the sodium ion can
transfer to the sulfur electrode in the solid electro-
5 lyte. The sodium ion, which has moved from the solid
electrolyte into the sulfur electrode, excites the
sulfur existing in the anode. The excited sulfur is
going to absorb the surrounding free electrons so as
to change itself to a bivalent negative ion, and at this
10 time it generates potential energy of about 2.08 volts.
The smooth supply of electrons to the anode is indis-
pensable for continuously maintaining such reaction of
battery. Therefore, in the anode a felt-like carbon
fiber, which has large surface, high non-corrosiveness
15 and good permeability of electron, is disposed to retain
the sulfur by impregnation. In such anode, since
sodium polysulfide which has high metal-corrosiveness
is produced with the progress of battery reaction, a
chromized steel which has high non-corrosiveness against
20 the sodium polysulfide, is used for a container ⁴ of the
anode active substance.

As mentioned above, the sodium transfers from
the inside of the ~~solid electrolyte tube~~ to the outside
at the time of discharge reaction of battery. There-
25 fore, the discharge of battery terminates when the
sodium is used up. At the time of charge, on the
contrary, the sodium polysulfide in the anode is
decomposed into the sodium ion, the sulfur and the

1 electron, and the sodium ion transfers in the solid
electrolyte in accordance with the electric field
produced by the voltage applied to the external circuit,
and returns into the cathode. That is, the electrical
5 capacity of the sodium-sulfur battery is determined by
the quantity of sodium existing in the cathode. If
the operating temperature of battery is low, the sodium
polysulfide produced at the time of discharge reaction
is solidified, and therefore the internal resistance
10 increases and the energy efficiency is reduced. On the
other hand, if the temperature is too high, the
troubles of high-temperature corrosion, thermal stress
and so on are caused. Therefore, the operating temper-
ature of 300°C to 350°C is suitable.

15 At the operating temperature as mentioned
above, the resistivity of β "-alumina which is the solid
electrolyte is about 3 to 5 Ω cm. The internal resist-
ance of battery consists of the resistances of the solid
electrolyte, anode portion and cathode portion. As to
20 the structure of the cathode portion, it is important
for improvement of efficiency to make the internal
resistance lower, and it is particularly important to
flow the sodium ion uniformly over the region of the
solid electrolyte. The reason is that the solid elec-
25 trolyte has the property deteriorated by electric
current and the rate of deterioration is proportionate
to the density of electric current. That is, in the
portion where the electric current flows more than

1 the other portions the electrolyte is damaged more, and
the life of the whole solid electrolyte is defined by
the portion where the current is concentrated. In order
to flow the electric current uniformly over the region
5 of the solid electrolyte, it is necessary that all of
the cathode surface of the solid electrolyte is in
contact with the sodium. However, since the quantity
of sodium in the cathode is increased or decreased by
the charge or discharge reaction, the liquid surface of
10 sodium changes. Therefore, in the embodiment the
cathode tube 5 is disposed in the solid electrolyte
tube to form a double tube structure and in addition
the region between the cathode tube and the solid
electrolyte tube is filled with metal fiber 9. As to
15 the metal fiber, a felt of stainless material, diameter
of which is not more than 30 μm , is preferable because
it has good wettability to sodium, hence the effect of
capillarity is enhanced, and also it has good non-
corrosiveness. The sodium is absorbed upward by surface
20 tension in the metal fiber and is supplied to all of the
internal wall of the solid electrolyte.

When the battery which has the above structure
is manufactured, the sodium as the cathode active
substance is injected into the solid electrolyte through
25 a sodium injection tube 10, and then it is enclosed.
Though the sodium to be injected is produced in advance
by eliminating K and Ca by purification methods such as
distillation and adsorption methods, these impurities

1 are existing in large quantities on the ground and
there is a great possibility that the impurities adhere
to the surface of the cathode component material. In
fact, in the battery which does not have the structure
5 according to this invention, as a result of checking
up the solid electrolyte after the charge and discharge
of about 100 cycles, the amount of Ca as the impurity
increased about four times. That is, the impurities
intermingled in the cathode at the time of manufacture
10 move in the solid electrolyte with the sodium and are
captured therein. These impurities are built-up in the
solid electrolyte by replacing the sodium which forms a
crystal of the solid electrolyte. At that time, the
change of component causes change of the crystal
15 structure of the solid electrolyte and deformation of
the crystal. Therefore, stress is generated in the
electrolyte to cause micro-cracking. In addition, since
the solid electrolyte in which the impurities are built-
up increases the resistance, it deteriorates in
20 efficiency to become unsuitable for practical use even
if it would not be broken. Accordingly, a method of
enclosing in the cathode a substance for eliminating
impurities is desirable for manufacturing the battery
which is good in performance and life.

25 In the embodiment of Fig. 1, the elimination
of impurities as mentioned above is realized by an
adsorbing action of porous amorphous carbon 12 which is
disposed in the bottom of the cathode tube 5. The carbon

1 was manufactured by The Fluorocarbon Company, Anaheim,
California 92803, U.S.A. Though there are various kinds
of porous amorphous carbon now, one having a specific
surface area of $2500 \text{ m}^2/\text{g}$ was used. When the specific
5 surface area is so large as above, the amount of the
carbon to be used can be much smaller. The reason is
that an ability of adsorbing the impurities is propor-
tionate to the surface area of carbon material. When
the above material was used, the impurities were
10 eliminated satisfactorily (0.5 ppm, a limit of detec-
tion, or less) only by use of about 50mg of carbon per
100g of sodium.

As the carbon materials which have large
specific surface area, there is provided a graphite felt
15 material which can be obtained by heat treating a raw
material of fiber at 2500°C or more. However, this
can't give an effect comparable to the amorphous carbon
because of smaller specific surface area by one figure,
lower purity and so on.

20 In use of the amorphous carbon in sodium, it
is important that the whole body of the carbon is in
the sodium in addition to the maintainance of high
purity as mentioned above. Since the amorphous carbon
has small pores and air bubbles or the like can't
25 easily escape upward if it adheres to the carbon, there
is a possibility that the carbon floats on the liquid
surface of sodium. If the amorphous carbon floats,
the surface area of the carbon in which it is in contact

1 with the sodium is reduced, so this is undesirable.
Accordingly, it is required to always secure the carbon
in the sodium. In the embodiment, a holding projection
13 secures the carbon in the bottom of the cathode
5 tube. This position is set in a path through which
the sodium is fed to the solid electrolyte tube, and
also in a place where the sodium flows with the electric
charge and discharge. In addition, it is most prefer-
able as a position where the carbon is disposed because
10 the carbon keeps in contact with the sodium until the
discharge terminates. When the sodium moves in the
place where the carbon exists, the impurities which are
eliminated fundamentally by diffusion can also be
eliminated by flow effect through a filter, thus the
15 above disposition of carbon is preferable for elimination
of impurity.

The sodium-sulfur battery which has the
structure as mentioned above continues stable charge
and discharge without increase of internal resistance
20 even if the charge and discharge are generated at more
than a few hundred cycles. On the contrary, in the
battery which does not use the amorphous carbon the
increase of internal resistance is remarkable, and it
is found, as a result of analysis and check up after
25 examination, that the amount of impurities in the solid
electrolyte increased. That is, the performance and
life of battery can be improved by elimination of
impurities through the amorphous carbon.

1 As set forth hereinabove, according to this
invention, it is possible to adsorb the impurities in
sodium to be harmless, and therefore the deterioration
of solid electrolyte is prevented so that the life of
5 battery can be remarkably extended.

CLAIMS:

1. A sodium-sulfur battery comprising sodium as a cathode active substance (2) and molten sulfur or molten sodium polysulfide impregnated to a porous and electrically conductive material as an anode active substance (3), which
5 effects electrochemical reactions of said cathode active substance (2) and said anode active substance (3) to charge or discharge through a solid electrolyte (1) having conductivity only for sodium ion, characterised in that a porous adsorbent (12) is immersed in said sodium as cathode active
10 substance (2).
2. The battery of claim 1, wherein said porous adsorbent (12) is a substance having a function of adsorbing to a surface thereof alkali metal except sodium and/or alkali earth metal which have electrochemically positive polarity
5 and act as an impurity in sodium.
3. The battery of claim 2, wherein said porous adsorbent (12) is porous amorphous carbon.
4. The battery of claim 2, wherein said impurity in sodium is potassium ion (K^+) and/or calcium ion (Ca^{2+}).
5. The battery of claim 1, wherein said porous adsorbent (12) immersed in said sodium is disposed near the closed bottom of tubular solid electrolyte (1) filled with said sodium as cathode active substance (2).

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FIG. 1

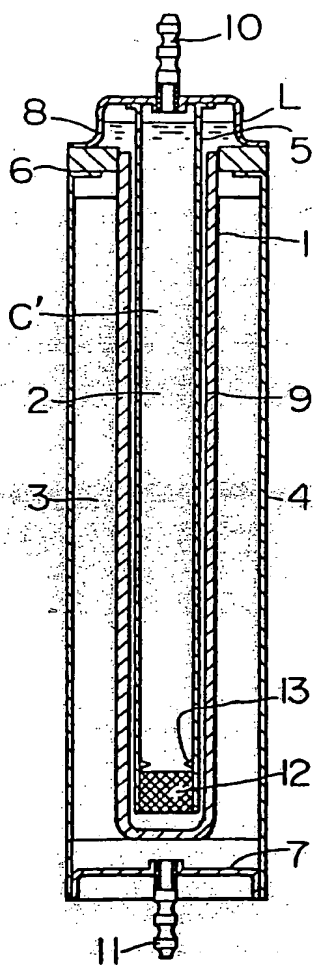


FIG. 2

